

BCS superconductivity of Dirac electrons in graphene layers

N. B. Kopnin^{1,2} and E. B. Sonin³

¹*Low Temperature Laboratory, Helsinki University of Technology, P.O. Box 2200, FIN-02015 HUT, Finland*

²*L. D. Landau Institute for Theoretical Physics, 117940 Moscow, Russia*

³*The Racah Institute of Physics, Hebrew University of Jerusalem, Israel*

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Possible superconductivity of electrons with the Dirac spectrum is analyzed using the BCS model. We calculate the critical temperature, the superconducting energy gap, and supercurrent as functions of the doping level and of the pairing interaction strength. Zero doping is characterized by existence of the quantum critical point such that the critical temperature vanishes below some finite value of the interaction strength. However, the critical temperature remains finite for any nonzero electron or hole doping level when the Fermi energy is shifted away from the Dirac point of the normal-state electron spectrum. We analyze the behavior of the characteristic length scales, i.e., the London penetration depth and the coherence length, which determine the critical magnetic fields.

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Graphite attracts attention of experimentalists and theorists for a long time. The interest is explained by unusual properties of this quasi-two dimensional material, which are mostly related with the existence of the Dirac or conic point in the electronic spectrum (see Fig. 1). Though the theory has predicted the existence of such point in graphite many decades ago[1], only recently the experimental evidences of its existence were received: first in graphite[2], which is believed to be a stack of weakly coupled atomic layers, and soon after it in graphene[3, 4]. The latter discovery has triggered an avalanche of experimental and theoretical works. Moreover, graphene can display unusual properties as a part of normal-superconducting hybrid structures: For example, the Andreev reflection has been predicted to have new features not characteristic for typical contacts[5].

Thorough investigation of graphite has revealed also evidences of intrinsic superconductivity in doped samples (see Refs. [6, 7] and references therein). Various mechanisms of superconductivity in graphene have been considered theoretically. Phonon and plasmon mediated mechanisms were discussed in Ref. [8] whereas a resonating valence bond model was proposed in Ref. [9]. The Cooper pairing in the undoped graphene may experience problems because the Fermi surface shrinks near the Dirac point and reduces to zero the number of states at the Fermi energy. Indeed, it was shown within the BCS model[10] that the superconducting transition in the undoped graphene possesses a quantum critical point at a finite interaction strength below which the critical temperature vanishes. However, one would expect that the electrons in graphene may become unstable towards formation of Cooper pairs for any finite pairing interaction if doping shifts the Fermi level away from the Dirac point because the behavior of electrons in the latter case bears more resemblance to that in usual metals. This idea has been qualitatively discussed in Refs. [8, 11] and verified within the resonating valence bond model in Ref. [9].

The aforementioned investigations of superconductivity in graphene or graphite (except for Ref. 10, where only the undoped case was considered) were done taking into account the specific details of each particular pairing mechanism. However, it would be worthwhile to perform the analysis in a more general form independent of a particular nature of the pairing mechanism. In the present Letter we apply the standard *s*-wave BCS model for the Dirac spectrum of electrons with a minimum number of parameters characterizing the pairing interaction, i.e., its intensity and the range of interaction in the momentum space. The values of these two parameters may vary depending on the mechanism. Such approach inevitably ignores some details and thus is less accurate. However, we hope that the loss of accuracy is compensated by a more general and transparent picture of the most essential features of the Cooper pairing in the systems with the Dirac spectrum.

In what follows we calculate the critical temperature, the superconducting energy gap, and the supercurrent as functions of the doping level and the pairing interaction strength. Without doping the critical temperature vanishes below some finite value of the interaction strength. However, the critical temperature is nonzero for any nonzero electron or hole doping level when the Fermi energy is shifted from the Dirac point of the normal-state electronic spectrum. This provides the quantitative basis for the earlier conjectures of Refs. [8, 11] and agrees qualitatively with the results of Ref. [9] for resonating valence bond model. Moreover, by analyzing the effect of the Dirac point on the supercurrent we demonstrate a novel feature that, as distinct from the usual superconductors, the supercurrent density is not proportional to the total number of electrons but is drastically decreased due to the presence of the Dirac point. Finally, we estimate characteristic length scales (penetration depth and coherence length), relevant for determination of the critical magnetic fields.

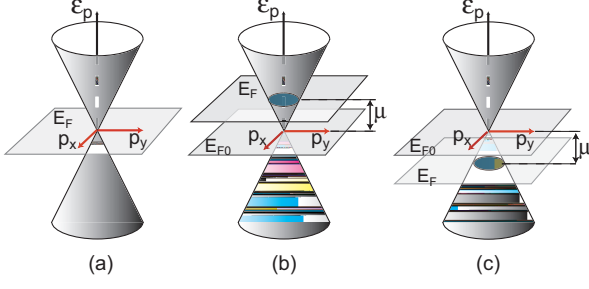


FIG. 1: (Color online) Conical energy spectrum. (a) Undoped, (b) electron-doped, and (c) hole-doped spectrum

Consideration of a two-dimensional model requires a few comments concerning the applicability of the mean-field approach. It is well known that the superfluid transition in a two-dimensional system occurs in the form of the Berezinskii-Kosterlitz-Thouless transition at a temperature lower than the mean-field transition temperature. Therefore our calculations provide the upper bound on the critical temperature and give a good estimate for the temperature scale of the transition [9]. Moreover, the applicability of the mean-field approach improves for graphite where a nonzero interplanar coupling, however small, does always exist.

Spectrum. – We assume the energy spectrum in graphene in the form

$$\epsilon_{\mathbf{p}} = \pm v \sqrt{p_x^2 + p_y^2} + E_{F0}.$$

The upper or lower sign refers to the conduction or valence band, respectively; E_{F0} is the Fermi energy without doping when the Dirac point lies at the Fermi level. If the Fermi energy is shifted by some amount μ due to doping, $E_F = E_{F0} + \mu$, (see Fig. 1) the energy measured from the Fermi level is

$$\xi_{\mathbf{p}} = \epsilon_{\mathbf{p}} - E_F = \pm v p - \mu.$$

The group velocity is $d\xi_{\mathbf{p}}/d\mathbf{p} = \pm v \mathbf{n}$ where $\mathbf{n} = \mathbf{p}/p$. For electron doping, $\mu > 0$, we have for $\xi_{\mathbf{p}} < 0$

$$p = \begin{cases} -(\xi_{\mathbf{p}} + \mu)/v, & \xi_{\mathbf{p}} < -\mu \\ (\xi_{\mathbf{p}} + \mu)/v, & -\mu < \xi_{\mathbf{p}} \end{cases}. \quad (1)$$

Similar relations take place in the case of hole doping, $\mu = -|\mu|$, as well.

BCS gap equation. – We use the standard BCS theory and assume an s-wave pairing interaction $V_p = -|V_p|$, where $|V_p| \sim |V|a^2$ is the Fourier transform of the pairing potential, V is the energy amplitude, and a is the range of interaction. We do not consider here the nature of pairing interaction, but refer the reader to Refs. [8, 9, 11, 12] where various possible mechanisms are discussed. The coupling constant λ is introduced through the equation

$$\frac{|V_p|}{2\pi\hbar^2 v^2} = \begin{cases} \lambda/\xi_m, & |\xi_{\mathbf{p}}| < \xi_m \\ 0, & |\xi_{\mathbf{p}}| > \xi_m \end{cases}.$$

Here ξ_m determines the interval where attractive interaction is present. In what follows we consider the case of low doping when $|\mu| < \xi_m$.

The BCS gap equation in a spatially uniform case is

$$1 = \frac{1}{2} \int |V_p| \frac{d^2 p}{(2\pi\hbar)^2} \frac{1}{E_p} [1 - 2n(E_p)], \quad (2)$$

where the energy of excitations is $E_{\mathbf{p}} = \sqrt{\xi_{\mathbf{p}}^2 + \Delta^2}$, the phase volume is $d^2 p = p dp d\phi$, where ϕ is the azimuthal angle of \mathbf{n} , and $n(E_{\mathbf{p}})$ is the equilibrium Fermi distribution of quasiparticles with energies $E_{\mathbf{p}}$. For zero temperature $1 - 2n(E) = \text{sign}(E)$. With help of Eq. (1), the BCS gap equation becomes

$$\frac{\xi_m}{\lambda} = \sqrt{\xi_m^2 + \Delta_0^2} - \sqrt{\mu^2 + \Delta_0^2} + |\mu| \ln \left[\frac{|\mu| + \sqrt{\mu^2 + \Delta_0^2}}{\Delta_0} \right] \quad (3)$$

for both electron and hole doping.

For zero doping $\mu = 0$ we have

$$\Delta_0 = \xi_m(\lambda^2 - 1)/2\lambda. \quad (4)$$

Nonzero Δ is possible only for the strong-coupling limit $\lambda > 1$ [10]. However, Eq. (3) shows that, for a finite doping, a finite Δ_0 exists even in the weak coupling limit $\lambda < 1$. In the case of low doping level when Δ_0 is small, Eq. (3) gives the gap in a BCS form

$$\Delta_0 = 2|\mu| \left(-\frac{\xi_m}{|\mu|} \frac{1 - \lambda}{\lambda} - 1 \right). \quad (5)$$

with the prefactor determined by the doping level $|\mu|$ rather than by the range of interaction.

Temperature dependence. – For a finite temperature Eq. (2) yields the gap equation

$$\frac{\xi_m}{\lambda} = 2T \ln \left[\frac{\cosh(\sqrt{\xi_m^2 + \Delta^2}/2T)}{\cosh(\sqrt{\mu^2 + \Delta^2}/2T)} \right] + |\mu| \int_0^{|\mu|} \tanh \frac{\sqrt{\xi^2 + \Delta^2}}{2T} \frac{d\xi}{\sqrt{\xi^2 + \Delta^2}}. \quad (6)$$

For $T \rightarrow 0$ we return to Eq. (3). Equation (6) leads to the equation for the critical temperature

$$\Phi(\xi_m/2T_c; \lambda) = F(|\mu|/2T_c) \quad (7)$$

where

$$\Phi(y; \lambda) = \lambda^{-1} y - \ln(\cosh y) \\ F(x) = x \int_0^x (x')^{-1} \tanh x' dx' - \ln(\cosh x)$$

where $F(x) > 0$. The critical temperature found from Eq. (7) is plotted in Fig. 2.

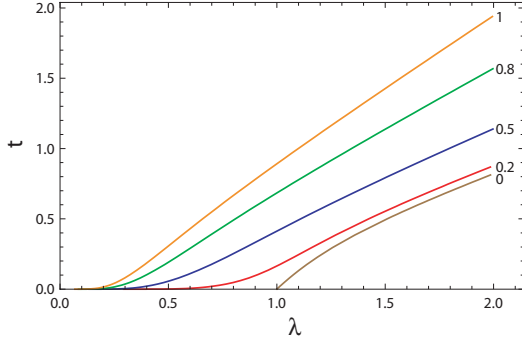


FIG. 2: (Color online) Normalized critical temperature $t = 2T_c/\xi_m$ as a function of the interaction constant λ for various doping levels $|\mu|/\xi_m$. The quantum critical point is at $\lambda = 1$ and $|\mu| = 0$.

For $\mu = 0$ the critical temperature satisfies $\Phi(\xi_m/2T_c; \lambda) = 0$, i.e.,

$$\xi_m/\lambda = 2T_c \ln [\cosh(\xi_m/2T_c)] . \quad (8)$$

This equation has a solution only for interaction strength above the quantum critical point, $\lambda > 1$ (see Fig. 2). If $\lambda \rightarrow 1$ we have $T_c = \xi_m(\lambda - 1)/2 \ln 2$ which vanishes at $\lambda = 1$. Comparing this with Eq. (4) we find $\Delta_0 = T_c 2 \ln 2$. In the other limit $\lambda \gg 1$ we find $T_c = \xi_m \lambda / 4$ and $\Delta_0 = 2T_c$. These results agree with Ref.[10] where only undoped case was considered.

However, for any low but finite doping level the critical temperature is finite. Consider weak coupling limit $\lambda \ll 1$ where we expect $T_c \ll \mu$. Indeed, the l.h.s. of Eq. (7) is $\Phi(y; \lambda) = y(\lambda^{-1} - 1) + \ln 2$ already for $T_c \ll \xi_m$. On the other hand, for $x \gg 1$ the r.h.s. of Eq. (7) is

$$F(|\mu|/2T_c) = \frac{|\mu|}{2T_c} \ln \left[\frac{2|\mu|\gamma}{e\pi T_c} \right] + \ln 2 . \quad (9)$$

where $\gamma = e^C = 1.78$ and $C = 0.5772$ is the Euler constant. This yields

$$T_c = \frac{2|\mu|\gamma}{\pi} \exp \left[-\frac{\xi_m(1-\lambda)}{\mu\lambda} - 1 \right] , \quad (10)$$

resulting in the BCS relation $\Delta_0 = (\pi/\gamma)T_c = 1.76T_c$.

Consider the vicinity of the quantum critical point $\mu = 0$ and $\lambda = 1$. On the weak coupling side $\lambda < 1$, the critical temperature is given by Eq. (10) which is exact provided $T_c \ll |\mu|$, i.e., for $1 - \lambda \gg |\mu|/\xi_m$. For $|\mu|/\xi_m \sim 1$ and $\lambda \rightarrow 1$, Eq. (10) works also reasonably well. For example, Eq. (10) gives $T_c \approx 0.42|\mu|$ for $\lambda = 1$. This can be compared to the exact value for $\lambda = 1$ which is found from the condition $F(|\mu|/2T_c) = \ln 2$ resulting in $T_c \approx 0.40|\mu|$. In the limit $\mu \ll T_c \ll \xi_m$ which is more appropriate on the strong-coupling side of the quantum critical point

$$T_c = \frac{\xi_m(\lambda - 1) + \sqrt{\xi_m^2(\lambda - 1)^2 + \mu^2 2 \ln 2}}{4 \ln 2} .$$

This holds for $|\mu|/\xi_m \ll \lambda - 1 \ll 1$, but also matches with the exact T_c by the order of magnitude when $\lambda \rightarrow 1$.

Therefore we come to the conclusion that a finite T_c does always exist for a finite μ . If $\lambda \gtrsim 1$, the critical temperature is close to that determined by Eq. (8) as long as $\mu \ll \xi_m$. If $\lambda \lesssim 1$ we essentially have Eq. (10).

Supercurrent. – Let us assume a homogeneous flow of the condensate: $\Delta = |\Delta|e^{i\mathbf{k}_s \cdot \mathbf{r}}$, where $\mathbf{k}_s = \nabla\chi$ is a constant gradient of the order-parameter phase. In the presence of magnetic field, $\mathbf{k}_s = \nabla\chi - (2e/\hbar c)\mathbf{A}$. Consider the state described by the particle-like and hole-like Bogoliubov-de Gennes wave functions

$$u(\mathbf{r}) = u_{\mathbf{p}} e^{i\mathbf{p} \cdot \mathbf{r}/\hbar} , \quad v(\mathbf{r}) = v_{\mathbf{p}} e^{i\mathbf{p} \cdot \mathbf{r}/\hbar} ,$$

where $\mathbf{p}_{\pm} = \mathbf{p} \pm \hbar\mathbf{k}_s/2$,

$$E_{\mathbf{p}} = E_D + E_{\mathbf{p}}^{(0)} , \quad E_{\mathbf{p}}^{(0)} = \sqrt{\xi_{\mathbf{p}}^2 + |\Delta|^2} ,$$

$E_D = (d\xi_p/d\mathbf{p})\hbar\mathbf{k}_s/2$ is the Doppler energy, and

$$u_{\mathbf{p}} = \frac{1}{\sqrt{2}}(1 + \xi_{\mathbf{p}}/E_{\mathbf{p}}^{(0)})^{1/2} , \quad v_{\mathbf{p}} = \frac{1}{\sqrt{2}}(1 - \xi_{\mathbf{p}}/E_{\mathbf{p}}^{(0)})^{1/2}$$

are the coherence factors. The standard expression for the current is

$$\mathbf{j} = 2e \sum_{\mathbf{p}} \left[\frac{\partial \xi_{\mathbf{p}+}}{\partial \mathbf{p}} |u_{\mathbf{p}}|^2 n(E_{\mathbf{p}}) - \frac{\partial \xi_{\mathbf{p}-}}{\partial \mathbf{p}} |v_{\mathbf{p}}|^2 [1 - n(E_{\mathbf{p}})] \right] . \quad (11)$$

Expanding Eq. (11) for small $E_D \ll \Delta, T$ and making shift in the momentum variable we find for the two-dimensional current density in the linear response regime

$$\begin{aligned} \mathbf{j} = e \int \frac{d^2 p}{4\pi^2 \hbar} \frac{\partial \xi_{\mathbf{p}}}{\partial \mathbf{p}} \left(\frac{\partial \xi_{\mathbf{p}}}{\partial \mathbf{p}} \cdot \mathbf{k}_s \right) \frac{\partial}{\partial \xi_{\mathbf{p}}} \left[\frac{\xi_{\mathbf{p}}}{2E_{\mathbf{p}}^{(0)}} [1 - 2n(E_{\mathbf{p}}^{(0)})] \right] \\ + 2e \int \frac{d^2 p}{4\pi^2 \hbar^2} \frac{\partial \xi_{\mathbf{p}}}{\partial \mathbf{p}} \left[n(E_{\mathbf{p}}) - n(E_{\mathbf{p}}^{(0)}) \right] . \end{aligned}$$

This yields the current

$$\mathbf{j} = (e\Lambda/4\pi\hbar)\mathbf{k}_s$$

where Λ is the characteristic energy. For zero temperature we have

$$\Lambda = 2|\Delta| + \frac{\mu^2}{\sqrt{\mu^2 + |\Delta|^2}} - \frac{|\Delta|^2}{\sqrt{\mu^2 + |\Delta|^2}} .$$

In contrast to the usual superconductors the supercurrent density is not proportional to the total electron density, being drastically affected by the presence of the Dirac point. In particular, for weak coupling limit, $|\Delta| \ll \mu$, the current $\mathbf{j} = e\mu\mathbf{k}_s/4\pi\hbar$ is proportional to $|\mu| \propto \sqrt{n}$, where n is the density of free carriers provided by doping. Near the quantum critical point when $T \ll \xi_m$, the

current is determined by the superconducting gap itself. Indeed, for zero doping, Eq. (11) yields

$$\Lambda = |\Delta| \tanh \frac{|\Delta|}{2T}.$$

For low temperatures, $T \ll |\Delta|$, we have $\mathbf{j} = e|\Delta|\mathbf{k}_s/4\pi\hbar$. Close to T_c , where $|\Delta| \ll T_c$, the current assumes the Ginzburg-Landau form $\mathbf{j} = e|\Delta|^2\mathbf{k}_s/8\pi\hbar T_c$.

Characteristic lengths and critical fields. – As usual the critical fields are determined by two spatial scales: the coherence length ξ_0 and the London penetration depth λ_L . At zero temperature the London penetration length for a graphene layer with thickness d is

$$\lambda_L^{-2} = \frac{2e^2\Lambda}{\hbar^2 c^2 d}.$$

It diverges near the quantum critical point $\lambda \rightarrow 1$, $\mu \rightarrow 0$. For the undoped case the London length is $\lambda_L = (\Phi_0/\pi)\sqrt{d/2\Delta}$, where $\Phi_0 = \pi\hbar c/e$ is the magnetic flux quantum. Close to the critical temperature the London length, $\lambda_L = (\Phi_0/\pi\Delta)\sqrt{T_c d}$, is inversely proportional $\sqrt{T_c - T}$ as in conventional superconductors. The coherence length has a standard form: $\xi_0 \sim \hbar v_F/\Delta$. Thus the Ginzburg-Landau parameter $\kappa = \lambda_L/\xi_0$, which characterizes the type of superconductivity, does not depend on the temperature near T_c as is the case in conventional superconductors:

$$\frac{\lambda_L}{\xi_0} \sim \frac{c}{v_F} \sqrt{\frac{T_c d}{e^2}}.$$

For typical values $v_F = 10^8$ cm/s, $d = 10^{-7}$ cm, and for $T_c \sim 1$ K, the Ginzburg-Landau parameter is on the border between the two types, $\kappa \sim 1$. Therefore, close to the quantum critical point where $T_c \rightarrow 0$ the superconductivity definitely becomes of type I.

To summarize, we have calculated the critical temperature, the superconducting gap, and the supercurrent as functions of the doping level and of the interaction strength for an s-wave pairing within the BCS model. The superconducting transition in the undoped graphene

has a quantum critical point with respect to the interaction strength, which disappears for any finite doping level such that a finite critical temperature exists for any weak pairing interaction. The amplitude of the supercurrent is drastically affected by the presence of the Dirac point, which leads to non-trivial behavior of the characteristic length scales (penetration depth and coherence length) determining critical magnetic fields.

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